# Absolute refractive indices and thermal coefficients of fused silica and calcium fluoride near 193 nm

Rajeev Gupta, John H. Burnett, Ulf Griesmann, and Matthew Walhout

The refractive indices of several fused silica and calcium fluoride samples from different suppliers were measured with the minimum deviation method in the deep UV between 191 and 196 nm with a standard uncertainty of 7 ppm. For both materials the dispersion $dn/d\lambda$ near 193 nm and 20 °C was determined. In addition, we measured the thermal coefficients of the refractive index near 193 nm and between 15 and 25 °C.

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## 1. Introduction

Recent developments in semiconductor lithography in the deep ultraviolet (DUV) at 193.39 nm, the vacuum emission wavelength of ArF excimer lasers, have made it necessary to obtain accurate data for refractive indices of optical materials in the DUV. Two important optical materials used in photolithographic exposure systems in the DUV are synthetic UV grade fused silica and calcium fluoride. To our knowledge, no measurement of the refractive index of either fused silica or calcium fluoride has been published for wavelengths below 200 nm. The most recent measurement of the refractive index of fused silica above 200 nm between 213 and 3710 nm was carried out by Malitson.[1] Those measurements were made with the minimum deviation technique. The accuracy of the indices of refraction were stated to be $\sim 10^{-5}$. Malitson also measured the temperature dependence of the refractive index in the same wavelength range. An upper bound for the thermal coefficient of fused silica at 184.9 nm has been published by Williams *et al.*[2] As in the case of fused silica, no data for the refractive index of calcium fluoride for wavelengths below 200 nm have been published. The most recent published refractive-index measurements are those of Malitson,[3] which start just above 200 nm and extend to nearly 9000 nm. The thermal coefficient of natural calcium fluoride from the DUV to the visible was measured at the beginning of the century by Micheli.[4]

We have measured the refractive indices of fused silica and calcium fluoride between 191 and 196 nm by using the minimum deviation technique in carefully controlled environmental conditions. In addition, we measured the thermal coefficient of both materials at 194 nm, the wavelength of a strong $Cu^+$ line, between 15 and 25 °C. Several prisms made of different grades of fused silica from several suppliers and two grades of calcium fluoride were used in our investigation.

## 2. Experimental Procedure

The minimum-deviation technique[5,6] is commonly used to measure absolute refractive indices of optical materials with high accuracy. A prism with a nominal apex angle $\alpha$ of 60°, made of either fused silica or calcium fluoride, is mounted on a goniometric spectrometer as indicated in Fig. 1. The beam of a He–Ne laser, which enters the goniometer through the entrance slit, S1, is used to align the prism so as to achieve a minimum in the deviation angle $\delta$. The turntable of the goniometer is then locked to a precise mechanical $\theta$-$2\theta$ drive that maintains the minimum deviation alignment of the prism while focusing mirror M2 is scanned from one spectral line to the next with a stepper motor and precision gear. A photomultiplier tube, mounted behind exit slit S2, is used as the detector. The refractive index of the prism material, $n_{\mathrm{mat}}(\lambda)$, at an air wavelength $\lambda$ relative to

The authors are with the National Institute of Standards and Technology, Gaithersburg, Maryland 20899. M. Walhout's permanent address is the Department of Physics, Calvin College, Grand Rapids, Michigan 49546.

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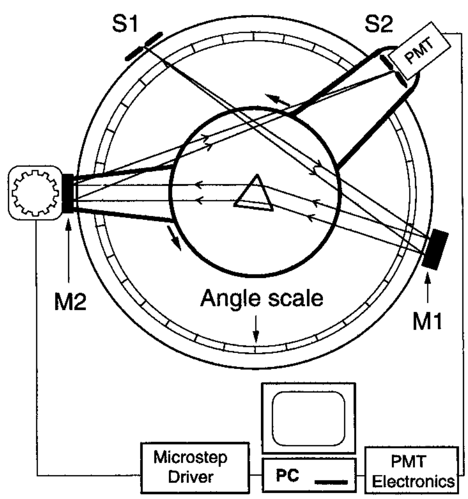


Fig. 1. Schematic of the Gaertner goniometric spectrometer equipped with reflective optics: $S_1$, entrance slit; $S_2$, exit slit; M1, collimating mirror; and M2, focusing mirror.

the index of the surrounding air, $n_{\mathrm{air}}(\lambda)$, is readily calculated with the following:

$$\frac{n_{\mathrm{mat}}(\lambda)}{n_{\mathrm{air}}(\lambda)} = \frac{\sin\left[\dfrac{\alpha + \delta(\lambda)}{2}\right]}{\sin\left(\dfrac{\alpha}{2}\right)},$$

once measurements of the apex angle $\alpha$ and the minimum deviation angle $\delta(\lambda)$ have been carried out.

The instrument used in our experiment is a precision goniometric spectrometer (built by Gaertner, U.S.A.). The spectrometer was originally designed for collimating and focusing quartz lenses in place of the concave mirrors, M1 and M2, shown in Fig. 1. The lenses were replaced by reflective optics to avoid problems caused by the strong chromatic aberration of quartz lenses in the DUV. As a result of mechanical limitations in the Gaertner spectrometer, it is not possible to observe the undeviated beam when the spectrometer is operated with reflective optics. The Gaertner spectrometer is therefore restricted to measurements of deviation angle differences for two wavelengths. Line radiation from a high-current CuNe hollow-cathode lamp, developed by Danzmann *et al.*,[7] is used to measure deviation angles in the DUV. Seven spectral lines in the vicinity of 193 nm are used for deviation measurements. The wavelengths of these lines are found in the compilation by Kaufman and Edlén[8] and are shown in Table 1. The wavelength uncertainty of the DUV lines is 0.1 pm or better. To obtain absolute deviation angles for the DUV lines, the differential deviation angles of the lines are measured first with respect to the deviation angles of four visible spectral lines from Hg, Cd, and He lamps (see Table 1). The wavelengths of the visible lines are taken from Reader *et al.*[9] Absolute deviation measurements for the same four visible wavelengths are then made with a second, refractive goniometric spectrometer (built by Wild, Switzerland), which enable us to convert the differential deviation measurements on the Gaertner spectrometer to absolute deviation angles. Although, in principle, one visible line is sufficient for determining the absolute deviation angle, four lines were used to reduce the uncertainty. A Hamamatsu photomultiplier tube with a GaAs photocathode is used as a detector, because it is sensitive in the visible and the DUV. The deviations at the visible wavelengths and the seven DUV lines from the hollow-cathode lamp are determined by scanning the spectrometer with a stepper motor coupled to the Gaertner spectrometer with a set of precision gears. Several scans of each spectral line are recorded on a computer. Since the recorded spectral lines resemble Gaussians, the line centers are determined by fitting a Gaussian to them to obtain the angular positions of the spectral lines. The standard uncertainty of the minimum deviation angle measurement is 1.9″. [Throughout the paper we employ the units degree (°), arcminute (′), and arcsecond (″) for angles.] We measure the apex angles of the prisms by mounting them on a goniometer and making a series of measurements of the orientation angles of the prism faces with an autocollimator. The entire surface of each prism face is illuminated by the autocollimator. Multiple measurements are made on both faces of each prism and are compared with a calibrated reference angle. The standard uncertainty of an apex angle measurement is 0.24″.

**Table 1. Spectral Line Wavelengths Used in Measurements**

| Spectral Line[a] | Emitter | Wavelength (nm) |
|---|---|---|
| Vis 1 | He | 587.562 |
| Vis 2 | Hg | 546.074 |
| Vis 3 | Cd | 508.582 |
| Vis 4 | Cd | 479.991 |
| UV 1 | $Cu^+$ | 195.75176 |
| UV 2 | $Cu^+$ | 194.45970 |
| UV 3 | $Ne^+$ | 193.88269 |
| UV 4A | $Ne^+$ | 193.00345 |
| UV 4B | $Cu^+$ | 192.97510 |
| UV 5 | $Cu^+$ | 192.21425 |
| UV 6 | $Ne^+$ | 191.60818 |

[a]We follow the usual convention whereby the wavelengths of the visible lines Vis 1 to Vis 4 are air wavelengths whereas vacuum wavelengths are used below 200 nm.

The refractive index determined by the minimum deviation technique yields the index of the material relative to the surrounding medium at ambient temperature, humidity, and pressure, which may change with time. Before measurements with the Wild spectrometer, the samples are allowed to come to equilibrium with the surrounding air.

Temperature, humidity, and pressure of the air are monitored during the course of the measurements. Measurements with the Gaertner spectrometer are carried out under strict environmental control. The spectrometer is enclosed in environmentally controlled housing where the humidity and the temper-

Table 2. Measured Refractive Indices of Fused Silica and Calcium Fluoride at 20 °C

| Sample | UV1 | UV2 | UV3 | UV4A | UV4B | UV5 | UV6 |
|---|---|---|---|---|---|---|---|
| | | | Fused Silica | | | | |
| A1 | 1.55706 | 1.55903 | 1.55991 | 1.56129 | 1.56133 | 1.56257 | 1.56355 |
| A2 | 1.55707 | 1.55904 | 1.55992 | 1.56131 | 1.56135 | 1.56257 | 1.56361 |
| A3 | 1.55707 | 1.55903 | 1.55992 | 1.56126 | 1.56136 | *not obs.* | 1.56354 |
| B1 | 1.55710 | 1.55906 | 1.55995 | 1.56133 | 1.56138 | 1.56261 | 1.56359 |
| B2 | 1.55709 | 1.55905 | 1.55994 | 1.56133 | 1.56137 | 1.56259 | 1.56358 |
| B3 | 1.55707 | 1.55904 | 1.55993 | 1.56132 | 1.56136 | 1.56257 | 1.56357 |
| C1 | 1.55705 | 1.55902 | 1.55991 | 1.56129 | 1.56133 | 1.56256 | 1.56355 |
| C2 | 1.55705 | 1.55901 | 1.55991 | 1.56129 | 1.56134 | 1.56256 | 1.56355 |
| | | | Calcium Fluoride | | | | |
| A1 | 1.49964 | 1.50087 | 1.50152 | 1.50229 | | *not obs.*[a] | 1.50369 |
| A2 | *not obs.* | 1.50088 | *not obs.* | 1.50233 | | *not obs.* | 1.50372 |
| B1 | *not obs.* | 1.50088 | *not obs.* | 1.50232 | | *not obs.* | 1.50371 |

[a]For several samples spectral lines are marked *not obs.* These lines were not used because of low signal-to-noise ratios.

ature are set to the same conditions prevailing during measurements with the Wild spectrometer of the same prism; the atmospheric pressure is monitored. The air index is calculated with the updated Edlén equation for the refractive index of air by Birch and Downs.[10] Since the air index is not a smooth function of wavelength below 200 nm owing to the Schumann–Runge absorption bands of oxygen, we have measured the refractive index of air in the DUV with a Chelsea Instruments UV Fourier-transform spectrometer at the wavelengths of the DUV lines that we used for the index measurements. The results confirm that the updated Edlén equation describes the air index with an accuracy of at least 1 ppm around 193 nm. Note that Peck and Reeder[11] have derived a formula for the dispersion of air that extends to wavelengths as low as 185 nm. Their formula is based on a few spectral lines of Hg in the UV of which only one is close to 193 nm. Once the refractive index of air is known, the absolute refractive indices of fused silica and calcium fluoride can be determined.

The temperature in the housing of the Gaertner spectrometer could be varied between 15 and ~30 °C. This temperature range enables us to measure the temperature coefficients of the refractive index of fused silica and calcium fluoride with good accuracy. The absolute deviation for the strong spectral line of $Cu^+$ at 194.54 nm was measured as a function of temperature in steps of ~2 °C to determine the temperature coefficient.

## 3. Fused Silica

The refractive indices of several grades of fused silica from three suppliers were measured for seven spectral lines UV1–UV6 between 191 and 196 nm. The results, normalized to a temperature of 20 °C, are listed in Table 2, and for one of the fused silica samples the index is plotted in Fig. 2. A quadratic polynomial, also shown in Fig. 2, was fitted to the experimental data to determine the refractive index of fused silica at the ArF laser wavelength of 193.39 nm by interpolation. The coefficients of the polynomial for one sample from a supplier are included in the last column of Table 3. The fitted polynomial was also used to determine the dispersion $dn/d\lambda$ of the samples at the same wavelength. For easier comparison the results for the refractive index of the fused silica samples are also shown in Fig. 3. It can clearly be seen that, although there is no statistically significant difference in the refractive indices between grades from the same supplier, there appears to be a difference of the order of 10 ppm between samples from different suppliers.

Our measurement of the temperature coefficient of the refractive index for fused silica is illustrated in Fig. 4. The refractive index was measured for the relatively strong $Cu^+$ line at 194.54 nm at six different temperatures comprising a temperature range of ~10 °C. The resulting temperature coefficient, $dn/dt$ between 15 and 25 °C, was found to be $(19.4 \pm 2.2) \times 10^{-6}$/°C. No temperature dependence of the temperature coefficient was observed within the temperature range covered by our experiment. An important advantage of the minimum-deviation technique for measurement of the index temperature coefficient over, e.g., interferometric

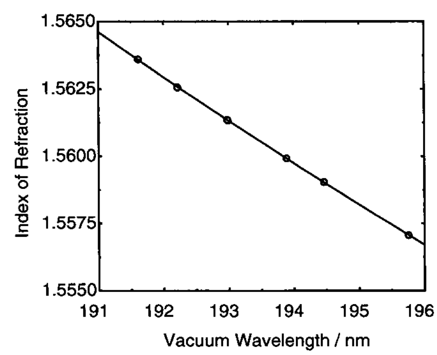


Fig. 2. Absolute refractive index of a fused silica sample as a function of wavelength between 191 and 196 nm at 20 °C. Uncertainties are too small to be shown with error bars.

Table 3. Refractive Index and Dispersion of Fused Silica at 193.39 nm[a]

| Sample | Index at 193.39 nm | Dispersion $dn/d\lambda$ ($nm^{-1}$) | Coefficients of $n(\lambda) = a_0 + a_1\lambda + a_2\lambda^2$ |
|---|---|---|---|
| A1 | 1.560685 | −0.001577 | $a_0 = 2.7361387$ |
| A2 | 1.560694 | −0.001587 | $a_1 = -1.0568836 \times 10^{-2}$ |
| A3 | 1.560683 | −0.001571 | $a_2 = 2.3221114 \times 10^{-5}$ |
| B1 | 1.560722 | −0.001577 | $a_0 = 2.5534849$ |
| B2 | 1.560714 | −0.001576 | $a_1 = -8.6907478 \times 10^{-3}$ |
| B3 | 1.560703 | −0.001577 | $a_2 = 1.8394076 \times 10^{-5}$ |
| C1 | 1.560676 | −0.001577 | $a_0 = 2.4949348$ |
| C2 | 1.560683 | −0.001578 | $a_1 = -8.0836337 \times 10^{-3}$ |
| | | | $a_2 = 1.6819456 \times 10^{-5}$ |

[a]Absolute refractive indices (column 2) and dispersions (column 3) at 193.39 nm of fused silica samples from three suppliers A, B, and C. The coefficients of a quadratic polynomial that was fitted to the refractive-index data between 191 and 196 nm for 20 °C are listed in the rightmost column. Since the refractive-index values for samples from one supplier are nearly equal, only the polynomial coefficients for the sample with the median index is tabulated. The uncertainty of the refractive index is $10.1 \times 10^{-6}$, corresponding to 7 ppm. The uncertainty in the dispersion is 2 ppm.

methods, lies in the independence of the deviation angle $\delta$ from the thermal volume expansion. In interferometric experiments both effects must be carefully distinguished.

Many factors contribute to the combined uncertainty of the refractive-index measurement. A detailed summary of all uncertainties is given in Table 4. Since the measurement procedure is identical for both fused silica and calcium fluoride, the analysis is valid for both materials. Note that one of the largest contributions to the uncertainty is caused by the difference in barometric pressure for the measurements with the Wild and Gaertner spectrometers for the same prism. The pressure is the only environmental parameter that cannot be controlled in the experiment.

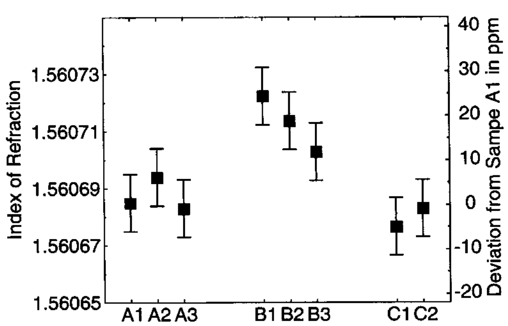


Fig. 3. Refractive indices of all measured fused silica samples at 193.39 nm and 20 °C from three suppliers (A, B, C).

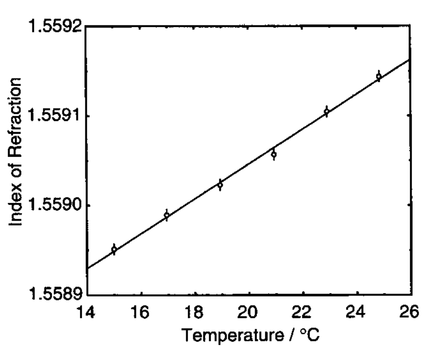


Fig. 4. Temperature dependence of the absolute refractive index of a fused silica sample at 194.5 nm. Between 15 and 25 °C the temperature coefficient $dn/dt$ is $(19.4 \pm 2.2) \times 10^{-6}$/°C.

Table 4. Uncertainty Budget of Refractive-Index Measurements

| Source of Uncertainty | Value | Index uncertainty |
|---|---|---|
| Apex angle measurement | 0.24″ | $0.8 \times 10^{-6}$ |
| Wild spectrometer measurement | | |
| Temperature uncertainty | 0.12 °C | $1.5 \times 10^{-6}$ |
| Deviation measurement uncertainty | 1.1″ | $3.6 \times 10^{-6}$ |
| Gaertner spectrometer measurement | | |
| Temperature uncertainty | 0.07 °C | $1.4 \times 10^{-6}$ |
| Deviation measurement uncertainty | 1.9″ | $5.9 \times 10^{-6}$ |
| Refractive index of air | | |
| Index uncertainty in DUV | | $0.2 \times 10^{-6}$ |
| Barometric pressure variation | | $7.0 \times 10^{-6}$ |
| Humidity variation | | $0.2 \times 10^{-6}$ |
| Combined index uncertainty ($1\sigma$) | | $10.1 \times 10^{-6}$ |

## 4. Calcium Fluoride

The measurements for calcium fluoride were carried out in the same way as those for fused silica. Table 2 contains the measured refractive indices, normalized to 20 °C, for the DUV lines. Lines UV4A and UV4B are unresolved because of the low dispersion of calcium fluoride in the DUV. In Table 5 and Fig. 5 the experimental results are summarized for the refractive index and the dispersion at 193 nm and 20 °C for a sample from each supplier. Our data show no difference in the refractive index between the samples from the two suppliers. We carried out three measurements of the temperature coefficient at

Table 5. Refractive Index and Dispersion of Calcium Fluoride at 193.39 nm[a]

| Sample | Index at 193.39 nm | Dispersion $dn/d\lambda$ ($nm^{-1}$) | Coefficients of $n(\lambda) = a_0 + a_1\lambda + a_2\lambda^2$ |
|---|---|---|---|
| A1 | 1.501939 | −0.00099 | $a_0 = 1.7865829$ |
| A2 | 1.501936 | −0.00099 | $a_1 = -1.9497270 \times 10^{-3}$ |
| | | | $a_2 = 2.4708935 \times 10^{-6}$ |
| B | 1.501924 | −0.00098 | $a_0 = 2.0409773$ |
| | | | $a_1 = -4.5899028 \times 10^{-3}$ |
| | | | $a_2 = 9.3206121 \times 10^{-6}$ |

[a]Absolute refractive indices (column 2) and dispersions (column 3) at 193.39 nm and 20 °C of calcium fluoride samples from two suppliers. A1 and A2 represent two measurements of the same sample A. Column 4 contains the coefficients of the second-order polynomial that were fitted to the data to obtain the refractive index in the range between 191 and 196 nm. These coefficients are valid for a sample temperature of 20 °C. The uncertainty of the refractive index is $10.1 \times 10^{-6}$, corresponding to 7 ppm. The uncertainty in the dispersion is 2 ppm.

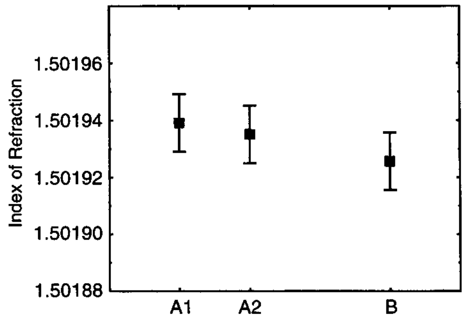


Fig. 5. Refractive indices of calcium fluoride samples at 193.39 nm and 20 °C from suppliers A and B. Here A1 and A2 represent two measurements of the same sample, A.

194.54 nm between 16 and 32 °C with two samples. The resulting averaged temperature coefficient at 194.54 nm and 20 °C is $(-2.9 \pm 0.3) \times 10^{-6}/°C$, in good agreement with the early measurement by Micheli.[3,4] Again, we did not observe a temperature dependence of the temperature coefficient.

## 5. Conclusion

We have carried out accurate measurements of the refractive indices of fused silica and calcium fluoride in the DUV at 193.39 nm. Dispersion and temperature coefficients for both materials at 20 °C were measured. Our refractive-index results for fused silica show statistically significant variations of the order of 10 ppm for samples from different suppliers. No variations in the refractive index between the samples from two different suppliers are observed for calcium fluoride.

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Commercial equipment, instruments, materials, or software are identified to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology or does it imply that the items identified are necessarily the best available for the purpose.

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